MOLECULAR SIMULATION STUDIES OF MEA ABSORPTION PROCESS FOR CO_2 CAPTURE

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Thesis submitted in partial fulfilment of the requirements
For the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2015

ABSTRACT

Concentration of CO_2 in the atmosphere is increasing rapidly. Emission of CO_2 directly impact on global climate change. Monoethanolamine (MEA) absorption process for CO_2 capture was developed to combat this trend due to its high reactivity. This allows higher priority absorption for carbon dioxide. The aim of this study is to investigate the intermolecular interaction between the solvent (MEA) and the acid gas (CO_2) during the absorption process. Molecular dynamic (MD) simulation will be used to study the molecular interaction and give insight of this process at molecular level. The intermolecular interactions for pure molecules (pure MEA, pure water, and pure CO2), binary system (MEA+CO2, CO2+H2O and MEA+H2O) and tertiary system (MEA+CO2+H2O) at different operating conditions are considered in this study. To perform the molecular dynamic (MD) simulation two boxes of carbon dioxide gas and MEA solvent are combined to study the absorption process. Thermodynamic condition under NVE, NPT and NVT conditions is specified in the simulation. The simulation results are analysed in terms of radical distribution function (rdf) to describe the intermolecular interaction and diffusion coefficient to calculate the solubility factor. Meanwhile, Mean square displacement (MSD) is also used to determine the diffusivity of molecules. The rdf function is plotted on the graph to identify the highest potential molecular interaction at various operating conditions. MD simulation was performed at temperature of 25^oC, 40^oC, and 45^oC to observe the potential interaction of molecules. The trend of rdf graph of each component shows an increasing trend with increase temperature. The purpose of studying primary system is to study the intermolecular interaction of each component on effects of different temperature. A further analysis of binary system was performed to study the intermolecular interaction between MEA molecule and H_2O molecule. The rdf graph generated from simulation proved that solubility of MEA in water increase with temperature. Hydroxyl group, –OH of MEA molecule interact with water to form hydrogen bonding bond. Tertiary system of intermolecular interaction is performed to study the CO_2 absorption in aqueous MEA solution. It is found that the amine group, -NH of MEA has higher probability to form carbamate ion with carbon dioxide compare to –OH group of MEA. As a references from binary system for tertiary system, higher number of lone pairs in hydroxyl group than amine group of MEA tends to form hydrogen bonds with water.

ABSTRAK

Kepekatan CO_2 dalam atmosfera meningkat dengan cepat. Pelepasan CO_2 memberi kesan secara langsung ke atas perubahan iklim global. Monoethanolamine (MEA) proses penyerapan untuk pengumpulan CO2 telah dijalankan untuk memerangi trend ini kerana kereaktifan yang tinggi. Ini membolehkan penyerapan yang lebih tinggi untuk karbon dioksida. Tujuan kajian ini adalah untuk menyiasat interaksi antara molekul antara pelarut (MEA) dan gas asid (CO2) semasa proses penyerapan. Molekul dinamik (MD) simulasi akan digunakan untuk mengkaji interaksi molekul dan memberikan wawasan proses ini pada peringkat molekul. Interaksi antara molekul bagi molekul tulen (MEA tulen, air tulen, dan CO2 tulen), sistem binari (MEA + CO2, CO2 + H2O dan MEA + H2O) dan sistem ketiga (MEA + CO2 + H2O) pada keadaan operasi yang berbeza dipertimbangkan dalam kajian ini. Untuk melaksanakan dinamik molekul (MD) simulasi dua kotak gas karbon dioksida dan MEA pelarut digabungkan untuk mengkaji proses penyerapan. Keadaan termodinamik bawah NVE, NPT dan NVT syarat yang dinyatakan dalam penyelakuan. Keputusan simulasi dianalisis dari segi fungsi taburan radikal (RDF) untuk menerangkan interaksi antara molekul dan resapan pekali untuk mengira faktor kelarutan. Sementara itu, Mean square displacement (MSD) juga digunakan untuk menentukan kemeresapan molekul. Fungsi RDF diplotkan pada graf untuk mengenalpasti interaksi tertinggi potensi molekul di pelbagai keadaan operasi. MD simulasi telah dilakukan pada suhu 25^{o}C, 40^{o}C dan 45^{o}C untuk memerhati interaksi potensi molekul. Trend graf RDF setiap komponen menunjukkan trend yang meningkat dengan peningkatan suhu. Tujuan belajar sistem pertama adalah untuk mengkaji interaksi antara molekul setiap komponen pada kesan suhu yang berbeza. Secara lebih terperinci sistem binari telah dijalankan untuk mengkaji interaksi antara molekul antara molekul MEA dan molekul H_2O. Graf RDF dihasilkan daripada simulasi membuktikan bahawa kelarutan MEA dalam air meningkat dengan suhu. Kumpulan hidroksil, -OH molekul MEA berinteraksi dengan air untuk membentuk hidrogen bon ikatan. Sistem ketiga dijalankan untuk mengkaji penyerapan CO_2 dalam larutan akueus MEA. Ia didapati bahawa kumpulan amina yang, -NH daripada MEA mempunyai kebarangkalian yang lebih tinggi untuk membentuk ion karbamat dengan karbon dioksida berbanding dengan kumpulan -OH MEA. Sebagai rujukan dari sistem binari untuk sistem ketiga, jumlah yang lebih tinggi daripada pasangan tunggal dalam kumpulan hidroksil daripada kumpulan amina daripada MEA cenderung untuk membentuk ikatan hidrogen dengan air.

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LIST OF ABBREVIATIONS

a_i	Acceleration
ε_o	Vacuum permittivity
ε_T	Relative permittivity
f_i	Force of Newton's second law of motion
m_i	Mass of particle
ρ	Density of atoms
r	Spherical radius
r_i	Change in particle position
$V(r_i)$	Potential energy respect to particle position
t	Time
∇_i	3 dimensions
Φ	Harmonic interaction force
Ψ_{nlm_l}	Wave function

Greek

Å	Amstrong
E	Energy
K	Harmonic force constant
M	Diffusion coefficient
N	Number of mole
N_i	atomic population
P	Pressure
P_{ii}	density matrix
S_{ii}	overlap matrix
T	Temperature
U_{AB}	Potential Energy
V	Volume

LIST OF ABBREVIATIONS

AO	Atomic orbitals
EIA	Energy information administration
DEA	Diethanolamine
MEA	Monoethanolamine
MD	Molecular dynamics simulation
MDEA	Methyldiethanolamine
MM	Molecular mechanic
MO	Molecular wave functions
MPA	Mulliken population analysis
MSD	Mean square displacement
QM	Quantum mechanic
RDF	radial distribution function
COMPASS	Condensed-phase optimized molecular potentials for atomic simulation studies
NPT	Constant number of moles, pressures and temperatures
NVE	Constant number of moles, volumes and energies
NVT	Constant number of moles, volumes and temperatures
LJ	Lernnard Jones potential
LPA	Löwdin population analysis
PBC	Periodic boundry condition (PBC)

1 INTRODUCTION

1.1 Motivation and statement of problem

Carbon dioxide is a well-known gases that are found everywhere in the atmosphere. In other country such as Canada and United State of America, greenhouse gas mitigation technology was introduced particularly with respect to increasing carbon dioxide in the light of climate change fears due to human activities (Rubin & De Coninck, 2005). Figure 1-1 shows the rise in global mean surface temperature and average temperature from 1961 – 1990 (Wessner, 2009). For the past 30 years, the growing in the concentration of carbon dioxide in atmosphere literally increases with the global temperature.

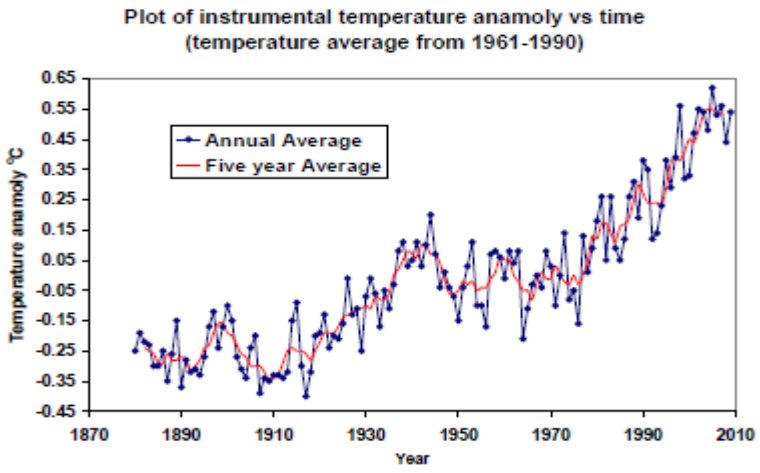

Figure 1-1: Plot of instrumental temperature anomaly versus time (temperature average from 1961 – 1990).

In US, 98% of greenhouse emissions is carbon dioxide in 2007, 40% is from electricity generation (Energy Information Administration, 2007). Most electricity generating sector such as fossil fuel power plant creates concentrated and large amount of carbon dioxide gas. The emissions of carbon dioxide in 2013 are about 32.5 billion metric tons. Energy Information Administration (EIA) estimates that the emissions of carbon dioxide will increase from 31 billion metric tons in 2010 to 36 billion metric tons in 2020, a 1.6% increase in every year (Energy Information Administration, 2013). Hence, there is an urgent need to deploy technologies that can utilize the fossil fuels in a cleaner way (less carbon dioxide released) to provide a bridge to a greener economy in

the future. MEA absorption process for carbon dioxide removal is the most promising technology available to stabilize the global climate change due to CO_2 emissions (Anusha, 2010).

1.2 Objectives

This research project aims to:

- Study the intermolecular interaction in monoethanolamine absorption process for carbon dioxide capture via molecular dynamic simulation technique at different process operating condition. The strength of intermolecular interaction between the CO_2 and the solvent will represent the absorption effectiveness.

1.3 Scope of this research

This case study cover few scopes,

- Molecular Dynamic (MD) simulation was used to study and give insight on the intermolecular interaction between solvent and acid gases in the absorption process.
- There are different systems at various operating conditions are considered in this study; pure molecules (pure MEA, pure water, and pure CO_2), binary system (MEA+CO_2, CO_2+H_2O and MEA+H_2O) and tertiary system (MEA+CO_2+H_2O).
- The optimum molecular interaction will be determined by observing the highest intermolecular interaction between molecular while simulating the absorption process at different temperature.
- Monoethanolamine act as the solvent while carbon dioxide is the acid gas. Since monoethanolamine is a primary amines and it is more effective for carbon dioxide removal compared to secondary and tertiary amines. It will form carbamate ions during the absorption process (Rajesh et al. 2006). The equation is:

  $$HOC_2H_4NH_2 + CO_2 \leftrightarrow HOC_2H_4NH_3^+ + HOC_2H_4NCOO^-$$ (carbamate)

The molecule interaction between MEA and carbon dioxide during the absorption process to form carbamate ion will be analysed and study through radial distribution function (rdf) graph.

- Mean square displacement is used to calculate the diffusion coefficient.

1.4 Main contribution of this work

This study gives insight on the molecular interaction between carbon dioxide and monoethanolamine during the absorption process. Meanwhile, the maximum intermolecular interaction occurred during the absorption process will be determined at various operating conditions.

1.5 Organisation of this thesis

The structure of the thesis is outlined as follow:

Chapter 2 presents the reviews of open literature of published researches which have been conducted in this regard. Brief explanation on amine based absorption process for carbon dioxide and reactivity of different types of alkanolamines is included in this chapter. The intermolecular interactions involved during the simulations and the thermodynamic properties used in this study also clearly explained in this chapter.

Chapter 3 describes the methodology applied in this study which includes the procedure and force fields specified in the simulation process. This chapter also explain the method to interpret radical distribution function into graphical form to analyse the intermolecular interaction between atoms.

Chapter 4 discuss the results obtained from the simulation. The results are interpreted to give insight on how the intermolecular interaction obtained from the molecular dynamic simulation will explain absorption process at molecular level.

Chapter 5 draws the summary of thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Introduction

This chapter discusses the carbon dioxide separation technologies, amine based absorption process, molecular dynamic simulation (MD) and modeling of molecules. The aim of this chapter is to review the fundamental science of the absorption process and the simulation technique.

2.2 Carbon dioxide separation technologies

There are several technologies available for carbon dioxide capture such as adsorption, membrane separation, cryogenic separation, physical and chemical absorption (Rackley, 2010). According to Zakkour and Cook 2010,

a) Membrane separation: Application of membrane separation typically a permeation process where carbon dioxide is absorbed into the membrane using polymer-based membranes, metallic membranes or ceramic membranes, then diffuse through it. In all cases, the pressure different across the membrane critically induce the flow across the membrane. So, membrane separation seldom uses for carbon dioxide capturing from flue gas which contained low CO_2 concentration and at low pressure.
b) Chemical solvents: Through this process, gas mixture is contacted with chemical solvent such as amines and alkanolamines in absorption tower. Most chemical solvent especially amines such as monoethanolamine (MEA) with smaller plant size is able to remove carbon dioxide at low concentrations and make the process suitable for low pressure, low carbon dioxide concentrations gas stream (Sada, Kumazawa, & Butt, 1976).
c) Physical sorbents: This process similar to chemical sorbent but the different is the way to absorb carbon dioxide as it utilize weak physical bond as opposed to chemical bonds used for chemical solvents. Zeolites and activated carbon are some of the examples of solid adsorbent used to separate carbon dioxide from gas mixtures (Young & Crowell, 1962).
d) Cryogenic separation process: The process involves using of distillation column which gas mixture is introduced at the based then it migrates up through the

column. Various fractions are then separate at different heights and dew points. High purity of carbon dioxide can be achieved using this technique but cryogenic separation technique has not achieved widespread commercial development (Jha, 2006).

2.3 Amine based absorption process

2.3.1 Process

There are many ways to capture carbon dioxide as previously mention. In this study, chemical solvent separation technology using monoethanolamine was selected since amine based absorption is more effective for carbon dioxide removal from flue gas (Chakrawarti et al., 2001).

This process involved a reversible reaction between a weak acid (CO_2) and a weak base (MEA) to form a soluble salt. Figure 2-1 shows the process flow diagram of the MEA based absorption process. In absorber, the inlet carbon dioxide is absorbed by the MEA. The solution enriched with CO_2 is then preheated before entering the stripper. After addition of heat, the reaction is reversed. From the bottom of the column, heat exchanges occur between the solvents and recycle back to the absorber. From the top, a high purity of carbon dioxide is produced (Alie, 2004).

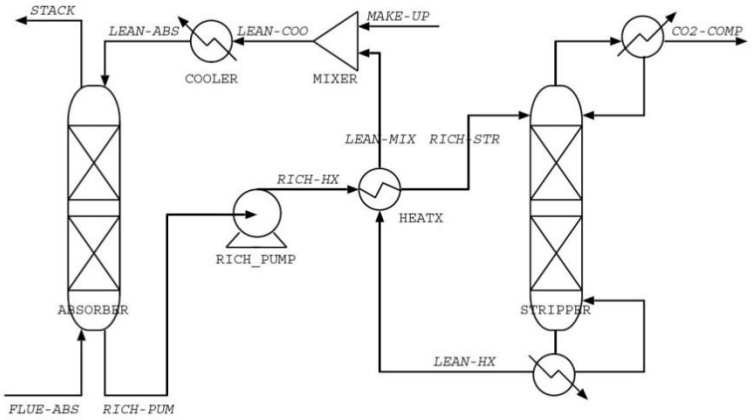

Figure 2-1: Process flow diagram for CO2 removal via chemical absorption

The advantage of amine based adsorption technology is it is a matured technology for carbon dioxide capture and has been used for many oil and gas industries. It is suitable for retrofitting of the existing power plants (Yu & Huang et al., 2012). Amine based absorption have alkanoamines which containing at least one hydroxyl group. It also helps

to reduce vapor pressure and increase their solubility in aqueous solution (Park & Yoon et al., 2006).

2.3.2 Categorization of Alkanolamines

According to Farmahini 2010, alkanolamines are considering in group of ammonia derivatives which consists of at least one hydroxyl group and one amine group. The amine group can be classified into three subcategories based on the number of substituents on the nitrogen atom. The three classes of alkanolamines are as as described:

a) Primary alkanolamines: The amine carries one ethanol group and two hydrogen atoms are directly bonded to the nitrogen atom. Monoethanolamine (MEA) is an example of this category.

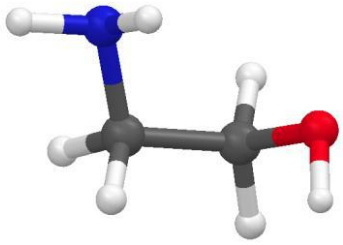

Figure 2-2: Molecular structure of monoethanolamine, C_2H_7NO

b) Secondary alkanolamines: In this category, each hydrogen from both side ends of the amine group has been replaced by ethanol group and only one hydrogen atom attached to the nitrogen atom. The best example is diethanolamine (DEA).

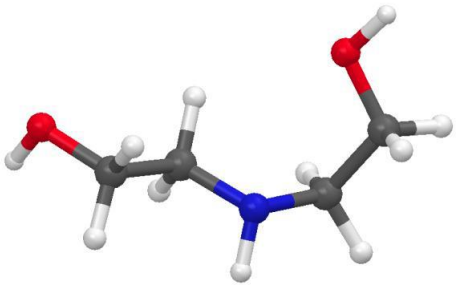

Figure 2-3: Molecular structure of diethanolamine, $C_4H_{11}NO_2$

c) Tertiary alkanolamines: These alkanolamines have one ethanol group at both end sides and no hydrogen bonded to the nitrogen atom. The hydrogen atoms have replaced by substituent groups which is the alkyl or alkanol groups. The best example is the methyldiethanolamine (MDEA).

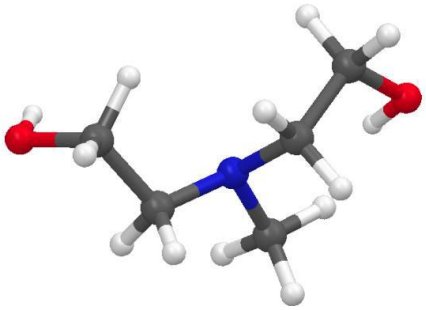

Figure 2-4: Molecular structure of methyldiethanolamine, $CH_3N(C_2H_4OH)_2$

2.3.3 Reaction between Amines and CO_2

Amine based absorption process technology is used to capture CO_2 in a large scale with amines as the solvent. There are three main type of amines can be used in absorption process. The three main types are primary amines (MEA), secondary amines (DEA) and tertiary amines (MDEA) (Nathalic et al., 2012).

The reaction between primary and secondary amines with CO_2 will form carbamate ion. Where else tertiary amines will form bicarbamate when react with CO_2. The reactions during the absorption process can be expressed as follows:

Primary or Secondary amines,

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+ + R_1R_2NCOO^- \ (carbamate) \quad (2.1)$$

Tertiary amines,

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow R_1R_2NH^+ + HCO_3^- \ (bicarbamate) \quad (2.2)$$

In comparison, primary and secondary amines have higher affinity for CO_2 and fast reaction. However, primary and secondary amines have higher regeneration cost due to carbamates formation. Formation of bicarbamates cause the tertiary amines requires lower regeneration cost. Although it has low regeneration cost, but the reactions are very slow and exhibit a lower affinity. Hence, primary and secondary amines were advance selected. Nowadays, the technology of catalyst was grown mature. Additional of small amount of activator to such a solution enhances the absorption process (Rajesh et al., 2006).

In this study, primary amines which is monoethanolamine (MEA) was selected to be used in the CO_2 capture process. There are a lot of advantages using MEA for the absorption process. MEA is primary amine which has smaller molecule size compare to other amines which make it easier to react. MEA has very low solvent and it is ease of

reclamation. MEA has low absorption of hydrocarbon. This shows that exist of other hydrocarbon would not affect the efficiency of CO_2 capture (Singh, 2011).

2.4 Molecular dynamic simulations

Molecular dynamic is a technique for computer simulation of complex systems which modeled at the atomic level. It gives the description of the atomic and molecular interaction that governs microscopic and macroscopic behaviors of physical systems. The connection can be shown in figure 2-5 (Cuendet & Michielin, 2008).

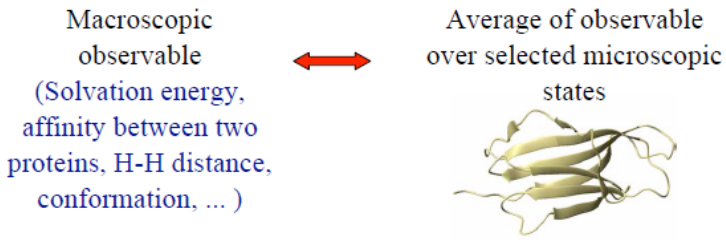

Figure 2-5: Connection between macroscopic world and microscopic world

Molecular Dynamic (MD) simulation depends on time evolution of the system. A microscopic replication of a macroscopic system constructed in a manageable box of molecules to study the configurations of the molecules and properties of the system in future. MD applied an initial configuration of molecules with calculated bond length, bond angle, force applied and other identities of the molecules as input. It is then computes the molecular forces based on the interaction parameter with a given force field. Newton's second law of motion is used to determine the velocities and molecules' position. The law is shown in Equation 2.3.

$$f_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} \tag{2.3}$$

The mass of the particle *I* is represented m_i, a_i is acceleration, t is time and f_i is the force acting on the particle which also can be calculation through the Equation 2.4 shown below where $V(r_i)$ is the potential energy respect to the particle's position.

$$f_i = \nabla_i V(r_i) \tag{2.4}$$

Data collected from previous proceeding step will be used to calculate new velocities and molecules' position after a very small time interval. MD generates a trajectory of the system with respect to time (Allen & Tildesley, 1987).

2.4.1 Molecular Dynamics Time Integration Algorithm

In MD simulations, Newton's second law of motion is used to calculate the time evolution of a set of interacting particles. From equation 2.3 where r_i in term of *t* can be express as $r_i(t) = (x_i(t), y_i(t), z_i(t))$. $x_i, y_i,$ and z_i ware the 3 direction of motion for a moving particle.

'Particles' corresponding to atoms, they represent distinct entitles such as chemical group that usually described in terms of interaction law. Integration of Equation 2.3 require information of instantaneous forces on the particle, initial positions and particle velocity to be solved numerically. MD trajectories are defined by both position and velocity vectors which describe the time evolution of the system in phase space. The position and velocities propagates in a finite time interval via numerical integrator. A good example for this is the Verlet, Velocity Verlet and Leapfrog algorithm (Jaroslaw, 2010). Verlet algorithm is the most common to be used in molecular dynamic simulations. Changing of particle position with time defined by $r_i(t)$, whereas the velocities $v_i(t)$ determine the temperature and kinetic energy in the system. The trajectories movement of the particles will be displayed and analysed with averaged properties (Farmahini, 2010).

Verlet algorithm from Taylor expansion is used to calculate the velocity explicitly which may affect the simulation with constant pressure. Modest operation mode and storage are required for velocity of Verlet. This allow the usage of a relatively long time steps duration as the position (r), velocities (v), and acceleration (a) are calculated at the same time with high precision using Equation 2.5.

$$r_i(t + \Delta t) \cong 2r_i(t) - r_i(t - \Delta t) + \frac{F_i(t)}{m_i}\Delta t^2 \qquad (2.5)$$

Besides this, the capability to conserve energy with numerically stable and time reversible properties becomes the reason for the software developer to use this algorithm (Farmahini, 2010).

2.4.2 Periodic boundary condition (PBC)

Periodic boundry condition (PBC) can be expressed as a periodic array of simulation boxes in every boxes surrounded by other replicated boxes in all directions. Figure 2-6 illustrate the two-dimensional representation of PBC.

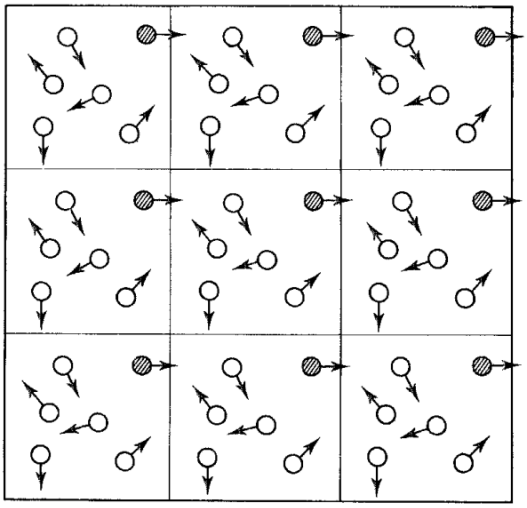

Figure 2-6: 2-D periodic boundary condition (PBC)

PBD is very useful to simulate bulk environment in limited number of molecules. It can be seen from figure 2-6 that if one molecule leaves the simulation box, the same molecule emerges from the opposite side of the box at the same time. Various shapes of PBC can be used in MD simulation. The shape of the periodic boundary condition depends on the configuration of the system. There are 5 shapes of periodic boundary condition to be used in MD simulation since they can fill all the space by translation operation of the central box in three dimensions such as simple cubic box, hexagonal prism, truncated octahedron, rhombic dodecahedron and elongated dodecahedron.

It is very important to decide the box size in the simulation. Simulation always carried out in a box. Hence, an appropriate fit with the dimension of the fluctuation or interaction should be chosen during simulation. As a case in point, short-range L-J interactions can be usually fitted into the boxes larger than on each side but this will be more problematic for long-range interactions (Leach, 2001).

2.4.3 Force fields

In molecular dynamic simulation, it applies the molecular mechanic concept with forces as important elements. Every potential energy functions are required to incorporate into force field concept to become the driving force of simulation. Force field can be divided into 3 generations. First generation generic force field which has a wide coverage to provides reasonable prediction of molecule structure which included all existent forces (Leach, 2001). Second generation improve the prediction quality rather than a wide applications. The third generation force field use quantum mechanical calculation to

produces the highest quality prediction which is very similar to actual condition and it can be applied to wide range of disciplines including biochemistry and materials science. Hence, it is important to select the right force field to give significant effect on the simulation result (Balbuena & Seminario, 1999).

In this study, the force field incorporates with both intermolecular and intra-molecular forces. COMPASS (Condensed-phase optimized molecular potentials for atomic simulation studies) is employed to simulate all the systems. This is because COMPASS is categorized as the third generation force field which is suitable in the simulation of organic molecule, inorganic gas molecule and polymers. The simulation qualities can achieve up to nearly same as the industrial process. COMPASS force field is a licensed force field which adds to the cross coupling term for the prediction of vibration frequencies and structural variation (Schlecht, 1998).

2.4.4 Thermodynamic Ensemble

A thermodynamical ensemble is a collection of microscopic states that all realize an identical macroscopic state. A microscopic state of system is given by a point (r, p) of the phase space of the system, where $r = (r_1, \ldots, r_N)$ and $p = (p_1, \ldots, p_N)$ are positions and the momenta of the N atoms of the system. There are three type of ensembles usually employed in MD simulations. The first type is NVE ensemble or microcanonical ensemble which fixed the number of particles (N), volume (V) and energy (E). The second type is the NPT or Isobaric-isothermal ensemble where the number of particles (N), pressure (P) and temperature (T) are fixed during the dynamic process through the usage of pressure and temperature controller. The third type is the canonical ensemble (NVT) which allows energy and pressure to be fluctuated (Allen & Tildesley, 1987) and is widely used in biological molecular simulations. Amongst these ensembles, NVE and NPT are the ensembles chosen to be applied in this study.

2.4.4.1 NVE

Equilibrium phase is the phase when the system evolves from the starting configuration to a stable or equilibrium system with energy conservation. In this study, NVE is used during this stage as this ensemble did not permit external forces to the system which is suitable to generate the state point of the system. The equilibrium stage will continue until the values of set monitored properties such as energy become stable, even though there is a possibility of energy drift during the ensemble generated (Rai, 2012).

2.4.4.2 NPT

NPT is chosen for this study as it imitates the experimental condition such as the requirement to have the correct pressure and temperature in the simulation (York, 2007). It is also suitable for large systems. In addition, the simulation under NPT is able to measure the equation of state for the system even if the viral expression for the pressure cannot be evaluated (Frenkel & Smit, 2002). The NPT ensemble has been used by Gunther et al. (2005) to collect the data of predicting the extractability of hydrophilic solutes by modified carbon dioxide extraction technique.

2.4.5 Analysis Parameter

The properties of MD simulations can be categorized into two parts which is the structure properties and dynamic properties. The structural properties are the object of the system which did not depend on time such as radical distribution function (rdf). While the dynamic properties of the system are fluctuate and time dependant properties. It calculates through time specified trajectory data such as mean square displacement (msd). However, this study only concern on the radial distribution function (rdf) as it can be used to give insight on the intermolecular interaction (Adam et al., 2013).

2.4.5.1 Radial distribution function

Radial distribution function (rdf) is an important structural property that basically used to characterize compound in general and Lernnard Jones potential (LJ). In particularly, rdf measure the probability of finding the neighbouring molecules at particular distance r from a reference molecule (Anslyn et al., 2006). Lernnard Jones potential (LJ) used to calculate the interaction potential between a pair of atoms. The rdf has the ability to be expressed in thermodynamic function such as in the internal energy E which is the sum of kinectic and potential energy, U as in Equation 2.6 (Hill, 1960).

$$E = \frac{3}{2}NkT + U \tag{2.6}$$

Integrating the Equation 2.6 will produce the potential energy, U and the equation can be rewritten as Equation 2.7.

$$\frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT}\int_0^\infty u(r)g(r,\rho,T)4\pi r^2\, dr \tag{2.7}$$

The radial distribution function can be defined by the Equation 2.8.

$$g(r) = \frac{1\langle N(r, r+dr)\rangle}{\rho 4\pi r^2 dr} \tag{2.8}$$

Where ρ is the density of atoms, r is the spherical radius, N is the number of atom. The rdf is important for three main reasons. Firstly, it is useful for pairwise additive potentials, knowledge of the rdf is sufficient information to calculate thermodynamic properties, particularly the energy and pressure. Secondly, the rdf is very well developed integral equation theories that permit estimation of the rdf for a given molecular model. Last but not least, the rdf can be measured experimentally, using neutron-scattering techniques. Figure 2-7 shows the schematic explanation of g(r) of a monoatomic fluid. The atom at the origin is highlighted by a black sphere. The dashed regions between the concentric circles indicate which atoms contribute to the first and second coordination number of shells respectively (Adam et al., 2013).

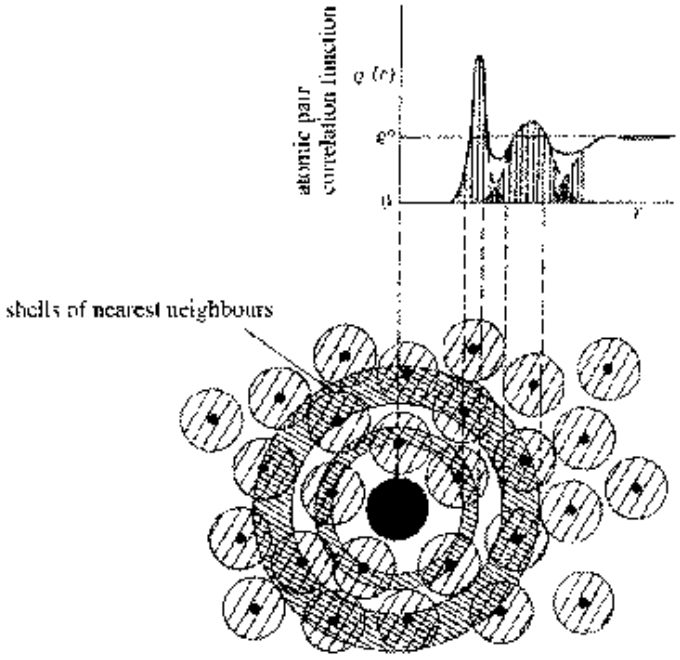

Figure 2-7: Schematic explanation of g(r) of a monoatomic fluid

The g(r) pattern basically depends on the phase of the system. The ideal gas will approach g(r) = 1. These patterns can be seen in Figure 2-7. Figure 2-7 (a) represents the g(r) in gas, (b) in liquid and (c) in solid phase.

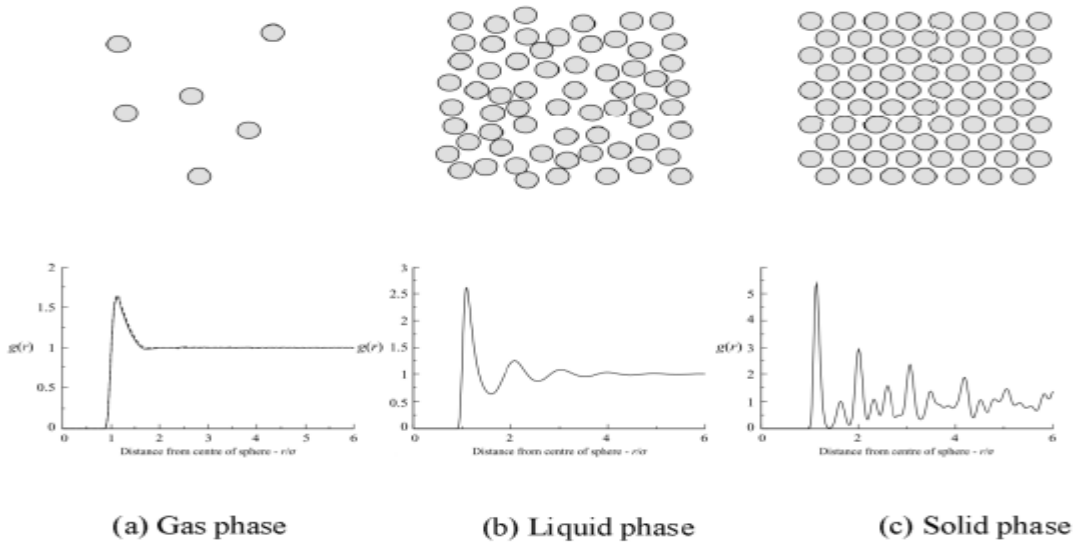

Figure 2-8: The atomic configuration and rdf pattern for (a) gas, (b) liquid and (c) solid phase (Barrat & Hansen, 2003)

From Figure 2-8, the rdf pattern for solid phase fluctuates more frequently as compared to liquid and gas phase. According to kinetic molecular theory of matter, the atoms of solid phase are arranged accordingly so they will vibrate constantly. Vibration between the atoms will cause repulsive force against each other. Therefore, many fluctuations occur as shown in Figure 2-8 (c). Since liquid atoms are just arranged closely to each other and gas atoms are far apart from each other, so their rdf patterns are quite stable as compared to solid phase.

2.4.5.2 Molecular Diffusion

Molecular Diffusion can be described as the spread of molecules through random motion. For a molecule M in an environment where viscous force dominates, its diffusion behaviour can be describe by the diffusion equation as below.

$$\frac{\delta}{\delta t} c(r,t) = D\nabla^2 c(r,t) \tag{2.9}$$

where $c(r,t)$ is a function that describes the distribution of probability of finding M in the small distance of the point r at time t. D is the diffusion coefficient and c is the concentration (Wang & Hou, 2012).

Molecular diffusion always related with the mean square displacement. Mean square displacement (MSD) of atoms in a simulation can be easily computed by its definition

$$MSD = \langle |r(t) - r(0)|^2 \rangle \tag{2.10}$$